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Blending of polymers offers attractive opportunities for achieving unique property combinations and for improving mechanical toughness but requires knowing how to control interactions to achieve miscibility or phase separated blends with proper interfacial coupling. Without controlled interactions, blends do not perform as desired and some strategy for compatibilization is necessary. Preformed block or graft copolymers may be added to act as interfacial agents or these may be formed in situ by reaction of suitably chosen functionalized polymeric components for control of phase morphology and the interface between these phases to obtain useful mechanical properties. This paper reviews some of the strategies currently being used to couple the phases in multicomponent engineering polymer alloys.

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Phase Coupling and Morphology Generation in Engineering Polymer Alloys

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Abstract

Blending of polymers offers attractive opportunities for achieving unique property combinations and for improving mechanical toughness but requires knowing how to control interactions to achieve miscibility or phase separated blends with proper interfacial coupling. Without controlled interactions, blends do not perform as desired and some strategy for compatibilization is necessary. Preformed block or graft copolymers may be added to act as interfacial agents or these may be formed in situ by reaction of suitably chosen functionalized polymeric components for control of phase morphology and the interface between these phases to obtain useful mechanical properties. This paper reviews some of the strategies currently being used to couple the phases in multicomponent engineering polymer alloys.

1. Introduction

The number of unique polymer molecules theoretically possible is almost without limit. The early years of the polymer industry were dominated by synthesis of new molecules to meet needs in the market place. The pace of developing new molecules has not stopped but it has slowed considerably since new chemistry is expensive and takes a long time to commercialize. Polymer blending or alloying has become an alternate route to new products and for problem solving [1]. In most cases, the reasons for selecting this approach fall into two categories: property combinations and cost dilution. Most products succeed because of a beneficial combination or balance of properties rather than because of any single characteristic. In addition, a material

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CONTENTS

Property Combinations

Chemical Resistance

Toughness

Cost Dilution

Cost

Performance

Δ = Formulation Cost

Figure 1. Illustrations of the concepts of property combinations and cost dilution via polymer blending.

Design of Engineering Polymer Alloys

- **Set performance objectives**
- **Formulation:**
  - Select major components
  - Compatibilization strategy
  - Process/composition optimization
  - Morphological analysis
- **Performance evaluation**

Figure 2.

must have a favorable benefit to cost relation to be selected over other materials for a particular application. These basic concepts are illustrated in Figure 1 using examples where the properties or performance of the blend are simple additive functions of the relative proportions of the two components A and B. A key technical issue is whether the blend will exhibit additive properties or not. In many cases properties are well below additive while in others they may be above additivity. The property relationships exhibited by blends depend critically on proper control of their phase behavior, and the following deals with some of the important issues in this area. The first is the selection or design of components when a homogeneous or miscible mixture is needed. The second involves phase separated systems where improved interfacial adhesion and morphological control are required, i.e., the concept of "compatibilization". The third deals with rubber toughening of brittle plastics and especially the issue of interfacial coupling and control of morphology. Copolymerization into random, block, or graft structures is a powerful way of dealing with all of these problems.

Figure 2 outlines the key elements required to design high performance engineering polymer alloys. The first step is to set the performance objectives which requires a thorough understanding of the application for the material. The middle step is to formulate a material that may meet these objectives while the last step is to evaluate the performance of various formulations. Steps 2 and 3 may be iterated until the desired objectives are achieved as suggested in Figure 3. This schematic attempts to define the boundary (dotted line) between formulation and performance evaluation. For multiphase blends the phase morphology and the coupling or adhesion between phases are the common features that link formulation and performance. This paper is most concerned with the formulation side of this process although clearly some measures of performance must be made to assess the value of any formulation. Relatively simple mechanical tests serve this purpose reasonably well in most cases.

Figure 3. Illustration of the interaction between formulation and evaluation steps to develop a polymer alloy to meet specified objectives.

2. Miscible Blends

Miscible blends are homogeneous to the polymer segmental level. Single phase blends are usually optically transparent and most physical properties will be at least as good as the composition weighted average of the pure components. In many ways, miscible blends are the physical equivalent of random copolymers made through chemical means. Very early in polymer science, it was concluded that miscibility among polymer-polymer pairs was a rare exception. However research over the last decade has proven this rule to be somewhat overstated [2]. The thermodynamic basis for miscibility in polymer blends is an exothermic heat of mixing since entropic contributions are so small in such systems. A major research thrust has been discovery of new miscible polymer blends. Significant advances have been made in understanding the origin of the interactions that govern miscibility, quantifying these thermodynamic parameters, and learning how to control them through molecular structure. The most obvious origin of exothermic mixing that could drive miscibility is specific interactions like hydrogen bonding [3]. When the interactions are not so directionally specific, mean-

field treatments seem to describe the essential behavior. Recent advances in this area for copolymer systems have occurred by appropriately accounting for both the intermolecular and intramolecular interactions between monomer units [4-6] using binary interaction models. When the intramolecular interaction is strongly repulsive, some copolymer compositions may prove to be miscible (a miscibility window) for systems where all homopolymer pairs are immiscible. Of course, intermolecular attraction can also lead to miscibility. These models provide a useful framework for quantitative molecular design of blends and are particularly useful for development of miscible blends involving functionalized polymers for reactive phase coupling as described below. Even though two polymers may be miscible at low temperatures, they often phase separate on heating because of a lower critical solution temperature. Control of phase diagrams for blends is then critical.

Thermodynamic interaction between components including miscibility is often a key element in the design of properly compatibilized multiphase alloys as will be illustrated in the following. Current research of the type described above provides a wealth of opportunities for formulating high performance engineering polymer alloys.

3. Immiscible Blends: Compatibilization

Immiscible blends have phase domains that consist, in the limiting case, of the corresponding pure components. Unlike composites, their phase morphology is not predetermined since all phases are fluid during processing. However, in many cases, there is a high interfacial tension between components in the melt that leads to an unstable and uncontrolled phase morphology and poor interfacial adhesion in the solid that leads to mechanical properties less than additive. As a result, such blends do not perform as desired and some strategy for compatibilization is necessary. Block or graft copolymers can be used to act as interfacial agents for solving these problems as suggested by the schematic models in Figure 4. This approach has been quite

successful as a means for designing impact modifiers for rubber toughening. Preformed block copolymers have been demonstrated [1,7,8] to effectively solve the compatibility problem for mixtures of immiscible plastics. Figure 5 illustrates the improvements in mechanical properties that can be achieved by adding appropriate block copolymers to physical blends of polystyrene (PS) and low density polystyrene (LDPE). However, the limitation for practical implementation of this approach is the lack of adequate chemical routes for economically producing block copolymers that would be appropriate for important systems.

An alternative is to form these blocks or grafts in situ during processing by reaction of suitably chosen functionalized polymeric components [9]. A particularly effective chemistry is the reaction of anhydride units with amine groups, e.g., at the ends of polyamide chains.
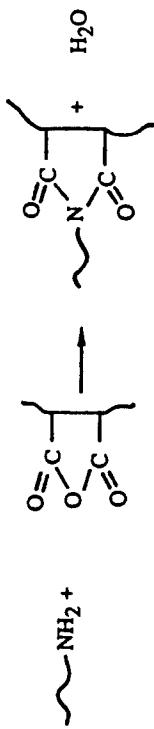
Reaction rates must be fast because the residence time in the melt processing equipment is only a few minutes at most and contact is limited to the interfacial regions between phases. The most obvious strategy for reactive compatibilization is to incorporate complementary functional groups (A and B) on each of the two polymers to be blended. However, this is often not convenient and Figure 6 illustrates a more attractive possibility. Here, one phase naturally contains functional groups B, e.g., polyamides, polyesters, etc., while the other has no inherent functionality. Functional groups A can be incorporated into this phase by addition of a functional polymer miscible with it. Of course, A and B can react at the interface to provide coupling. As illustrated in Figure 7, the nature of the interface between the two phases will influence the ease with which this reaction can occur.
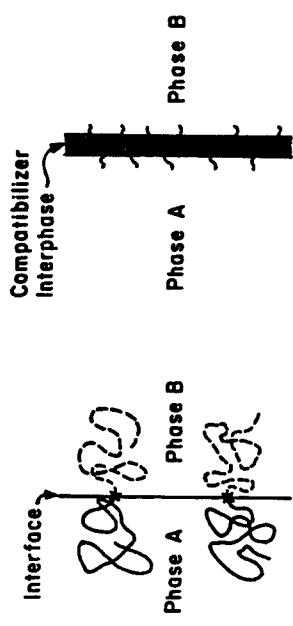

Figure 4. Illustration of ideal configuration of block copolymer at the interface (left) and of a compatibilizer forming an interphase (right) between polymer phases A and B.
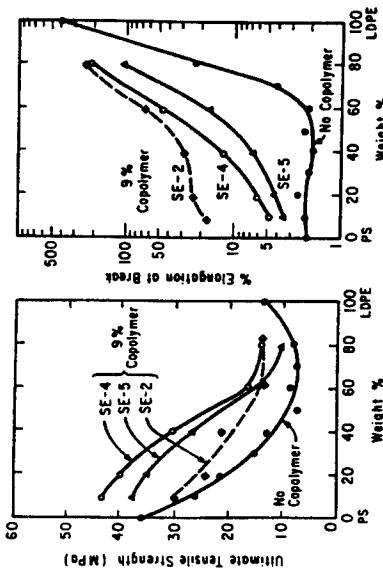

Figure 5. Effect of addition of block copolymers on mechanical properties of polystyrene - low density polyethylene blends.

in Figure 9 [4]. For a fixed SAN composition (dotted line in Figure 9 [4]), a range of SMA compositions fulfill the required miscibility. Figure 10 shows a measure of blend ductility versus nylon 6 content for blends with and without the reactive SMA in the ABS material (denoted as SAN-g in Figure 10). Without any compatibilization, the blends have mechanical properties well below that expected from additivity. With only 2% SMA in the SAN-g phase, the blends have ductility that is essentially additive. At slightly higher SMA levels, these blends are super-tough. A variety of other functional polymers can be added to the ABS material which are miscible with its SAN phase and which will react with the nylon. Figure 11 outlines some of the main issues associated with design of such reactive compatibilizers.

4. Rubber Toughening: Interfacial Coupling

Rubber toughening of brittle plastics involves a complex interplay of variables associated with the matrix, the rubber particles and the interface between these phases [10] as suggested in Figure 12. Here, the focus is on strategies for interfacial coupling of rigid and rubbery phases during melt blending and the related issues of morphology control.

A physical approach to phase coupling is to blend preformed elastomeric block copolymers (usually containing styrene blocks as a hard phase and diene-based blocks as a soft phase) with matrices like polystyrene, PS, or poly(phenylene oxide), PPO. Some possibilities are illustrated in Figure 13. Segment architecture and size are key issues for controlling phase morphology. Miscibility or physical interactions of the matrix material with the styrenic block provides interfacial adhesion. When the styrene blocks have a high molecular weight relative to the matrix, the rubber phase may form microdomains and these are usually too small for toughening. However, by using shorter blocks to control block copolymer rheology and interfacial interaction with the matrix, elastomeric macrodomains of a size and shape optimum for toughening can be formed.

Reactive Compatibilization

Condensation polymers
with reactive end groups:

nylons   NH$_2$, COOH
polyesters   OH
PC
PSF   ] phenolic
polyarylates   (?)
etc

Addition polymers
functionalized by:

copolymerization
grafting
end groups

Figure 6. Schematic illustration of reactive scheme for forming block and graft copolymers at the interface between immiscible phases in a blend of a condensation polymer having reactive ends and an addition polymer without functionality.


Sharp Interface   Diffuse Interface
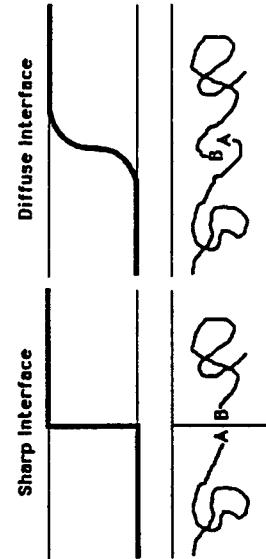
Figure 7. Reaction configuration at sharp and diffuse interfaces.

A strategy for reactively compatibilizing nylon 6/ABS blends is shown schematically in Figure 8 [9]. Polymer molecules that are miscible with the styrene/acrylonitrile copolymer, SAN, matrix and contain functional groups A (e.g., anhydride units) that can react with nylon 6 are used to effect phase coupling. One choice for the latter is styrene/maleic anhydride copolymers, SMA, since they form miscible blends with SAN for the composition range shown

Figure 10. Ductility of blends of nylon 6 and an ABS material (SAN-g) with and without reactive SMA copolymer for compatibilization.

Design of Reactive Compatibilizers

- Miscibility
- Functionality

graft vs block

Interfacial constraints
extent of reaction
effect on blend rheology
gel formation

- Molecular weight

diffusion to interface
phase anchoring
effects on component
properties (melt & solid)
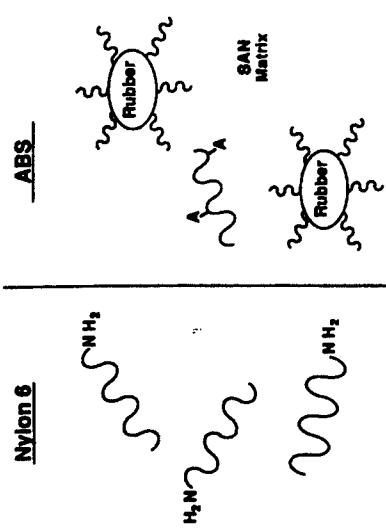
Figure 11.

Figure 8. Schematic showing reactive compatibilization strategy for nylon/ABS blends. The vertical line represents the interface between domains of the two materials.
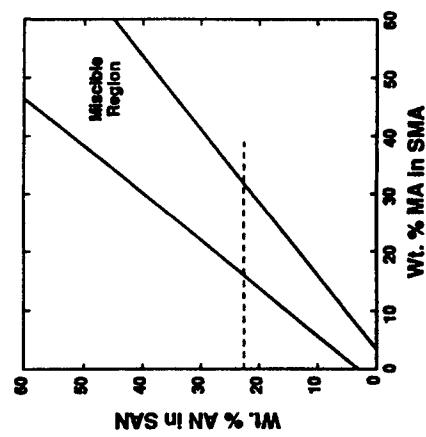
Figure 9. Miscibility map for the case where the reactive polymer added to ABS in Figure 8 is a styrene/maleic anhydride copolymer.

Alternatively, the rubber phase can be coupled to the matrix chemically as suggested in Figure 14. In this approach, functional groups are incorporated into a suitable rubber. Typically, maleic anhydride is grafted to an ethylene/propylene rubber or to a styrene/ethylene-butene/styrene thermoplastic elastomer. The functional groups react with the matrix, e.g., by amine end groups in polyamides, etc. In addition to causing adhesion, these grafting reactions lead to a powerful means of controlling the size of the rubber particles. Numerous studies have demonstrated the importance of phase dimensions on toughening polyamides [11-13]. Rheological factors, mixing intensity, and a variety of chemical issues all play important role in determining the morphology of such blends.

Reactive Coupling of Rubber to Matrix

grafted chains

Matrix (e.g. nylon)

Rubber: EPDM-g-MA
SEBS-g-MA

Figure 14. Reactive coupling of a functionalized rubber domain to a plastic matrix.

The routes suggested in Figures 13 and 14 require empirical adjustment of the chemical structure of the rubber and processing conditions to arrive at the optimum rubber phase morphology, e.g., particle size, for toughening of a particular matrix. Emulsion-made core-shell impact modifiers offer a means of precise and independent control of particle size [10]. The interfacial interaction with the matrix needed to achieve dispersion and adhesion can be achieved by either physical (Figure 15) or

Rubber Toughening

Matrix
- deformation mechanism
- intrinsic ductility

Particles
- size and distribution
- properties
  - modulus
  - crosslinking
 - glass transition

Interface
- adhesion
- dispersion

Figure 12.

Block Copolymers as Impact Modifiers

$M_{PS} >> M_{matrix}$

$M_{PS} << M_{matrix}$

PS

Matrix (e.g. PS or PPO)

TPE macrodomain

Rubber microdomain

Rubber particles too small for toughening

Figure 13. Domain structure of thermoplastic elastomer (TPE) block copolymers added to plastics for impact modification.

chemical (Figure 16) means. The chains that are grafted to the rubber core and that form the shell are typically PMMA-based or SAN copolymers. These may be miscible with the matrix, e.g., PVC, or wet it, e.g., polycarbonate. A third component can be added that will physically couple the shell and matrix. An example of this is shown in Figure 17 when polycarbonate, PC, is added to aid the dispersion of an impact modifier with a PMMA shell into poly(butylene terephthalate), PBT. Alternatively, the shell can be functionalized so that reaction occurs with the matrix. This functionality may be made part of the graft chains by copolymerization (left in Figure 16) or by physically adding a functional polymer that is miscible with the matrix (right in Figure 14).

The effectiveness of this approach is illustrated in Figure 18 where a styrenic copolymer containing 8 wt% maleic anhydride, SMA8, is used to disperse an impact modifier with a PMMA shell into a nylon 6 matrix. SMA8 is miscible with PMMA and is solubilized in the brush of PMMA chains that are grafted to the rubber core and the maleic anhydride groups can react with the nylon 6 to complete the coupling.

**Grafted Shell-Core Modifiers: Physical Coupling**

Miscible	Wetting/Adhesion	Wetting Agent (e.g. PC)
Shell = SAN or PMMA	PMMA	PMMA
Matrix = SAN or PVC	PC	Polyesters

Figure 15. Methods for physical coupling of core-shell impact modifiers to the matrix phase.

Grafted Shell-Core Modifiers: Reactive Coupling

Matrix (e.g. nylon)
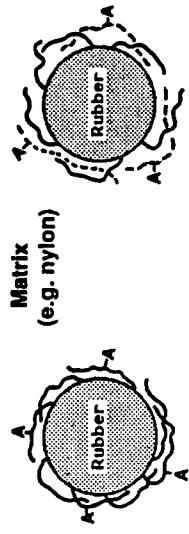
Functionalized grafted chains

Functional additive miscible with shell (e.g. SMA or SAA for PMMA shell)
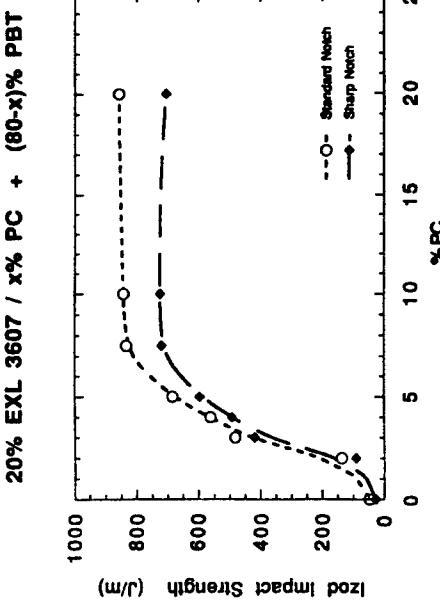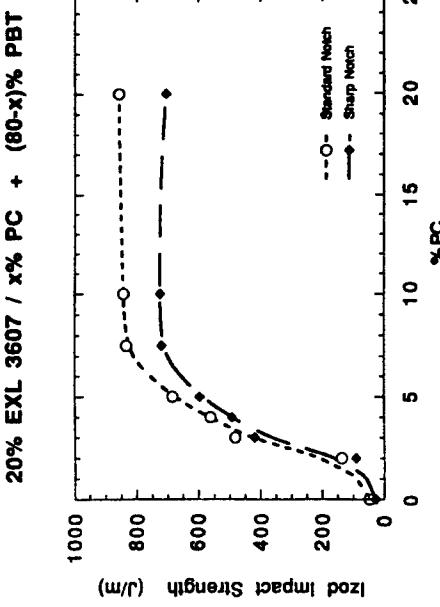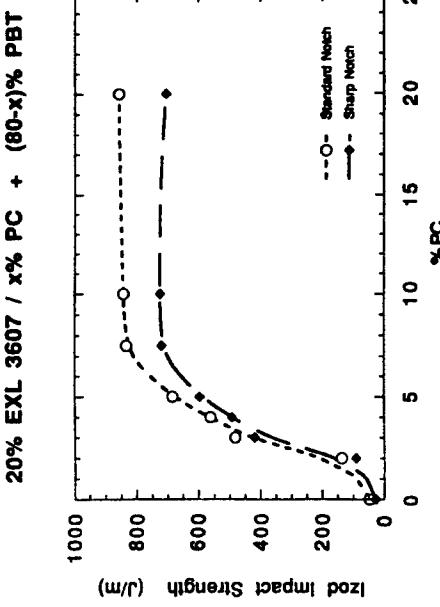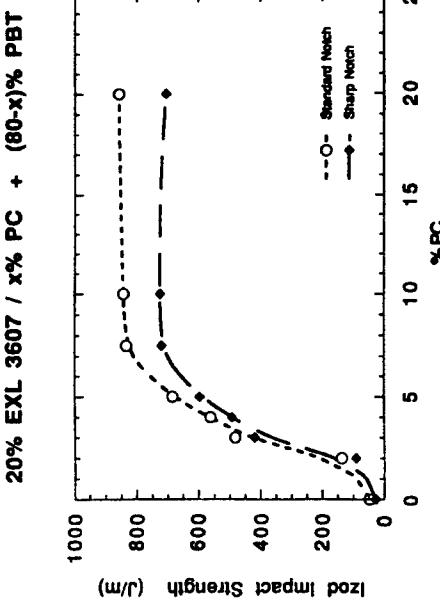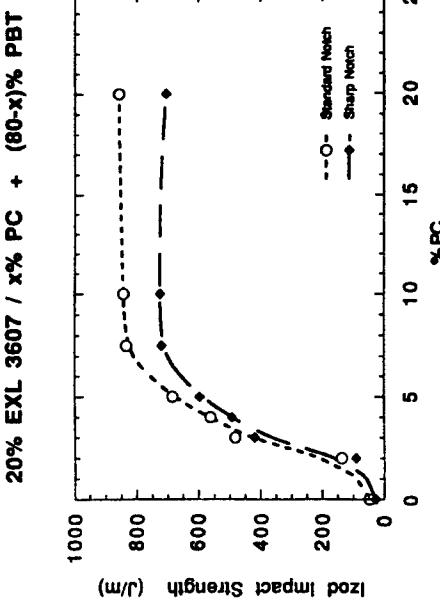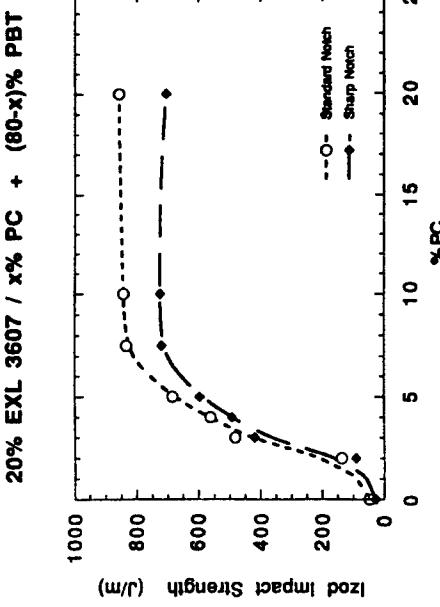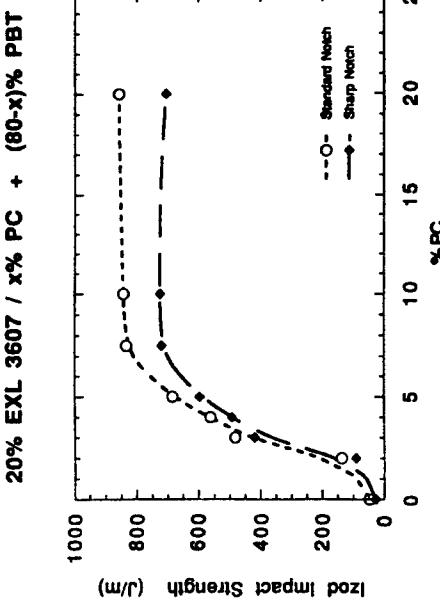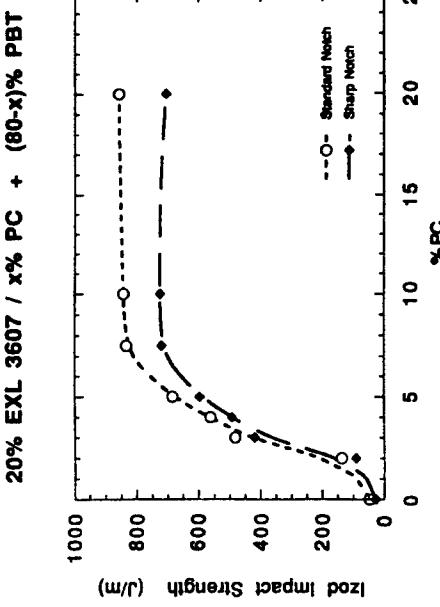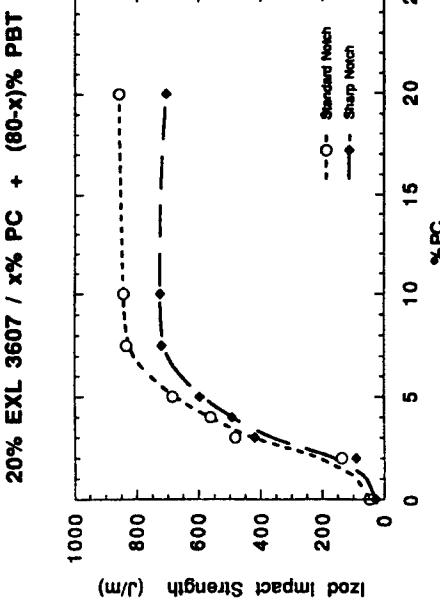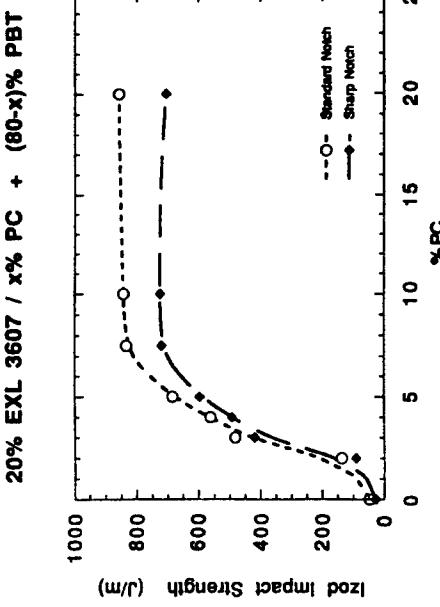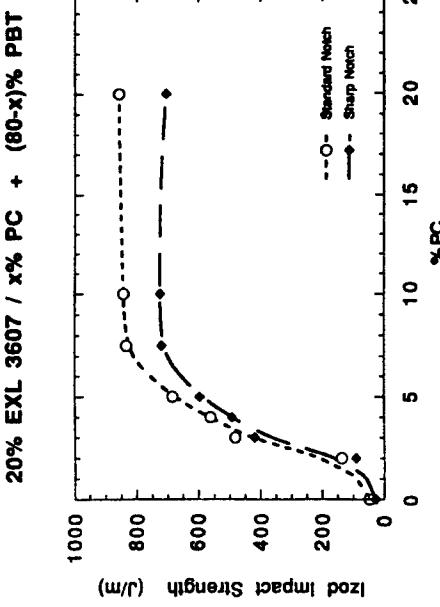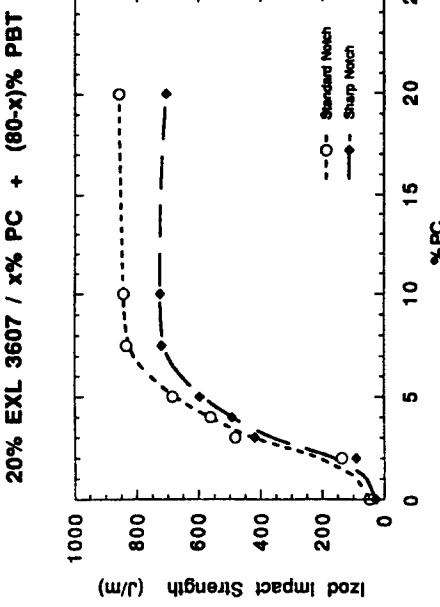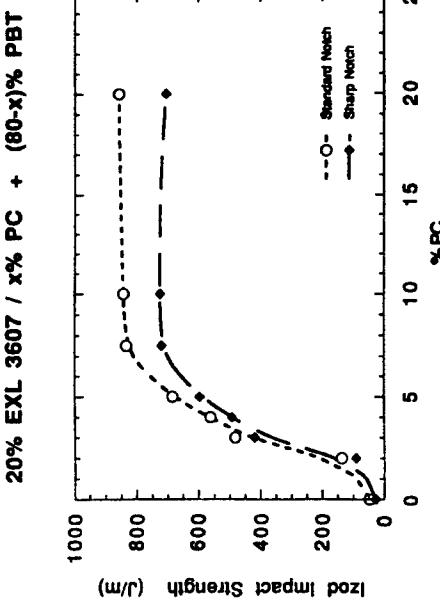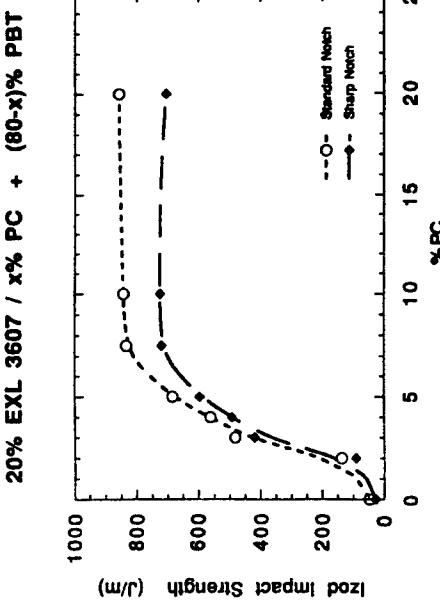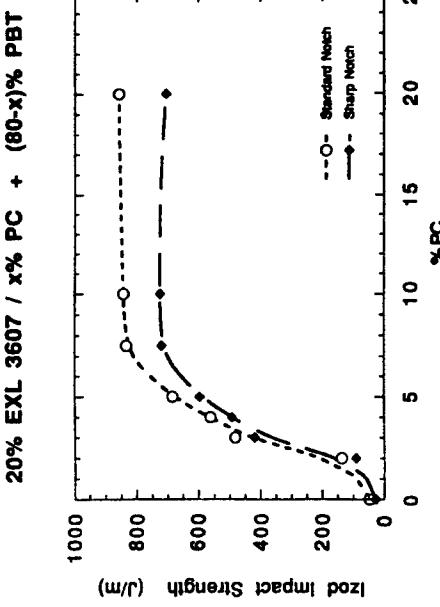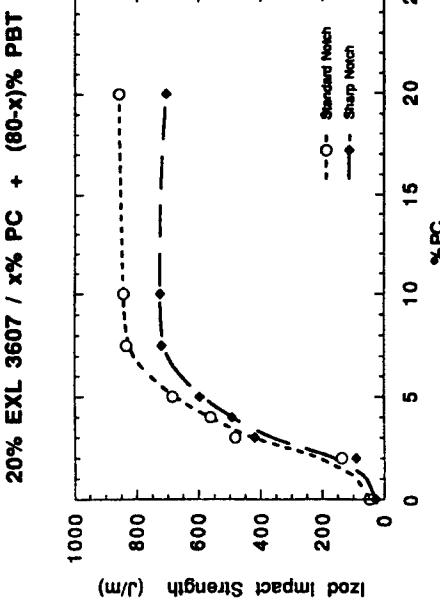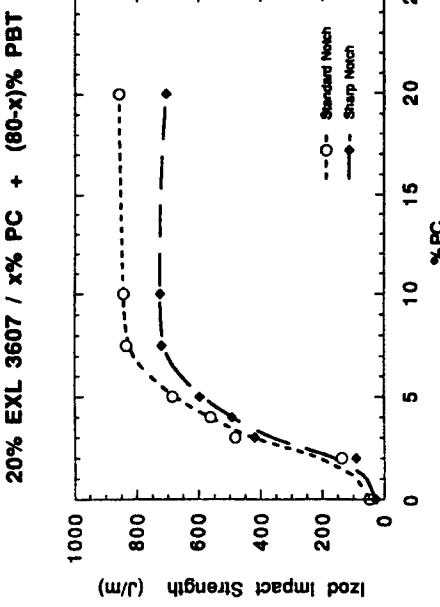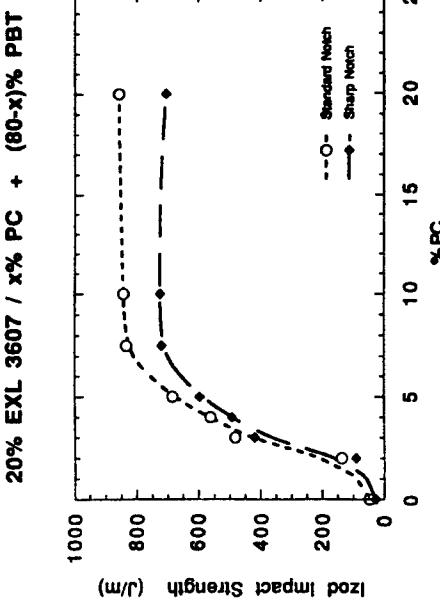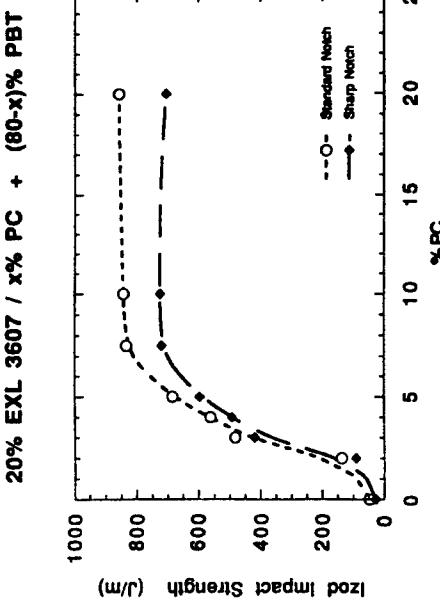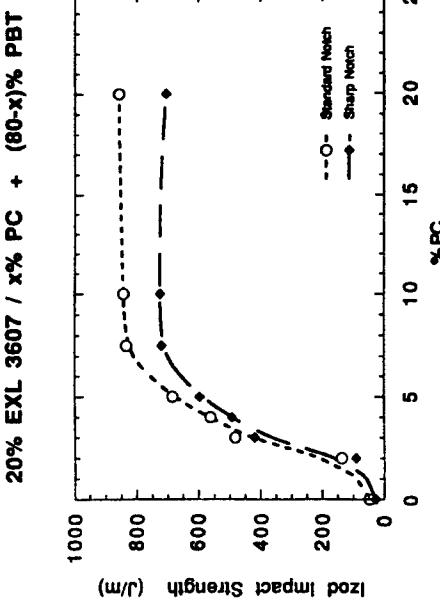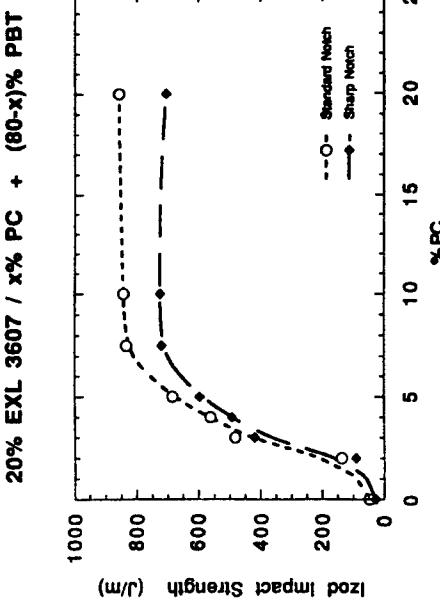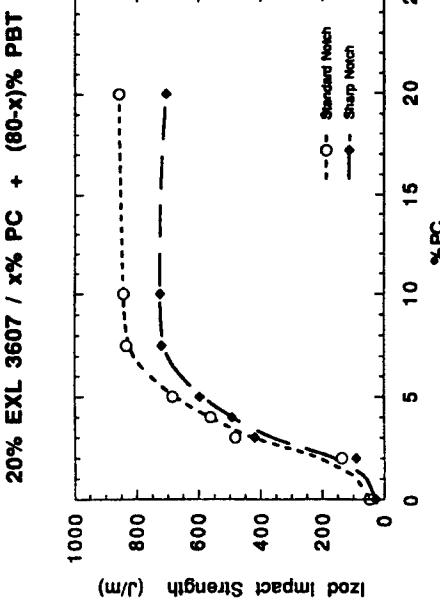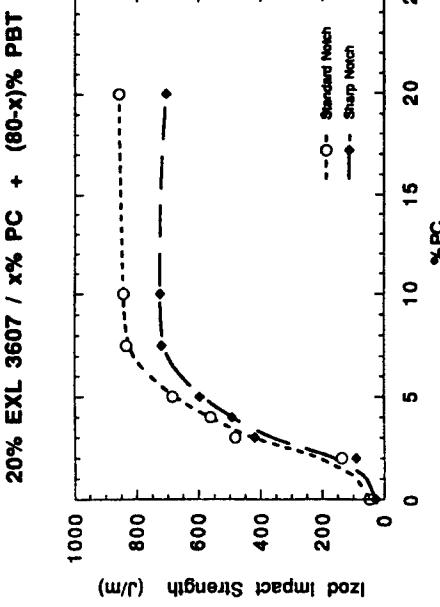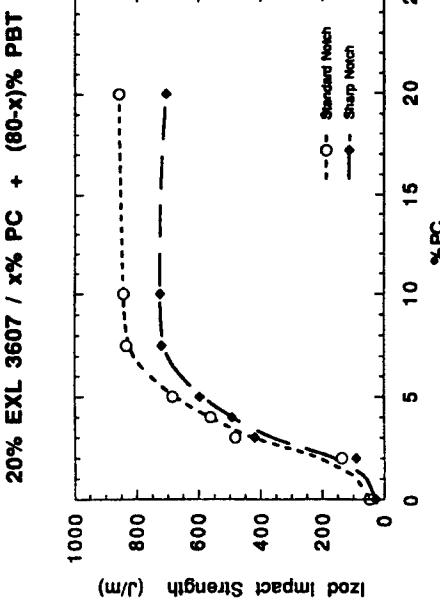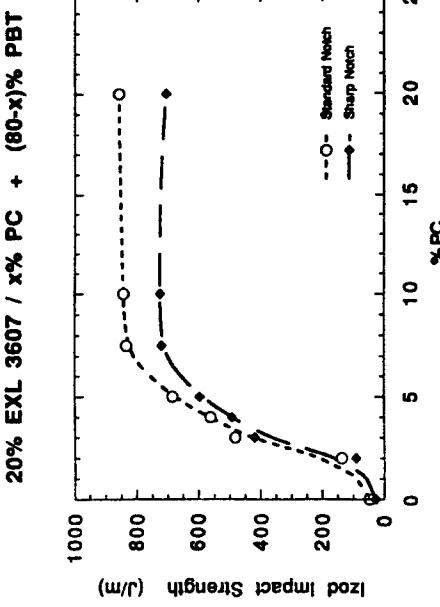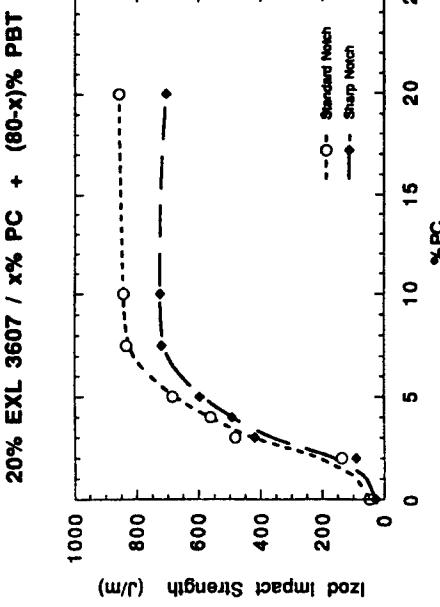
Figure 16. Schemes for chemical coupling for core-shell impact modifiers to the matrix phase.


20% EXL 3607 / x% PC + (80-x)% PBT

Figure 17. Use of polycarbonate as an aid for dispersing a core-shell impact modifier (EXL 3607) into a poly(butylene terephthalate) matrix.
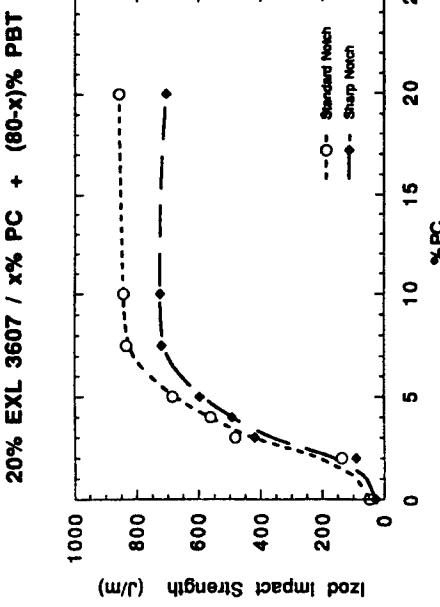
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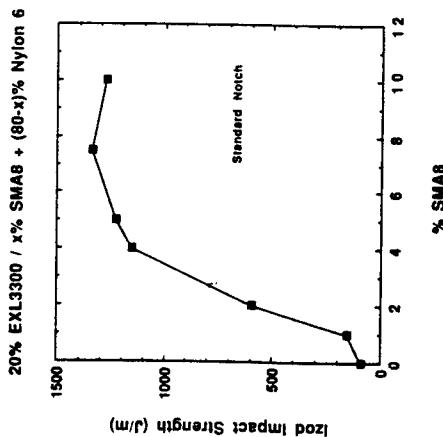
Figure 18. Use of a styrene/ maleic anhydride copolymer as an aid for dispersing a core-shell impact modifier (EXL 3300) into a polyamide matrix.

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